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TINTED GLAZE CONTAINING CHROMIUM-BEARING WASTE

M. T. Mukhamedzhanova,[1] A. P. Irkakhodzhaeva,[1] S. S. Ishankhodzhaev,[1] F. I. Érkabaev,[1] and S. Ishankhodzhaev[1]

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The possibility of using chromium-containing waste generated by galvanic production in preparation of tinted glazes is investigated.

The development of civil engineering and the increasing requirements of industrial aesthetics call for an expanded production volume and a wide range of facing materials.

The opacified glazes currently used in the industry contain substantial quantities of costly and scarce components. Therefore, the development of thermally and chemically resistant glazes based on commonly available components is of great significance. Such are opacified titanium glazes for facing tiles, which have high opacifying capacity, luster, microhardness, and thermal and chemical resistance. It has been established [1, 2] that in such compositions, titanium dioxide in combination with silicate compounds of bivalent metals produces a high degree of opacification and is an adequate replacement for zircon.

The purpose of the present study was to develop new compositions for tinted opacified glazes based on chromium oxide obtained from waste chromium solutions and to clarify its effect on the properties and opacification of titanium-bearing glaze coatings.

It is known that in long-term service of electrolytes in electric precipitation of chromium, the ions of iron and heavy metals accumulate in the solution and make the electrolyte unfit [3]. The regeneration and purification of such solutions have not brought successful results so far; accordingly, they have to be removed from the system. The use of such solutions in the production of various products and materials is economically justifiable.

Based on the studies performed, a technology for producing varnish and pigment materials to be used as paint fillers and pigments [4] was developed from waste chromium-bearing solutions generated by the galvanic production. This technology mainly includes three chemical processes: separation of ions of iron and heavy metals from the waste solution through neutralization; reduction of hexavalent chromium ions to trivalent ions, employing an organic agent (sawdust); synthesis of pigment by firing the chromium-containing mixture produced by evaporation of the reduced chromium-containing solution.

The technology for producing chromium-containing pigment is as follows. The waste chromium-containing solution (25 – 50 g/liter chromium) from a pressurized tank is pumped into a neutralization tank. Neutralization is carried out at pH = 5.0 – 5.5. In doing so, a substantial precipitate of hydroxides of iron and other heavy metals is formed. The precipitate is separated on a filter. The solid iron hydroxide with impurities after drying is directed toward the production of iron pigment. The filtrate is fed into a tank to reduce hexavalent chromium. Sawdust, being stirred, is poured into the reactor in the ratio 1 : 1 with respect to the quantity of chromium. Next, concentrated sulfuric acid is added in small quantities in the same ratio.

After 1.5 – 2 h of contact of the components, the solution is separated from the precipitate and sent into a tank for the separation of sulfate ions, employing calcium (or barium) hydroxide. Next, having filtered the calcium (or barium) sulfate precipitate, the filtrate is transferred to the evaporation device. Evaporation is carried out at a temperature of 50 – 70°C to a dry residue of chromium hydroxide. The obtained dry residue is fired for 1 h in a muffle furnace at a temperature of 800 – 900°C. The fired product is easily crushed in a ball mill. X-ray and thermographic analysis established that the obtained product is chromium trioxide.[2]

Tinted glazes are colored owing to selective absorption of light waves in the visible spectrum range, which is related to the different absorption coefficients for different wavelengths. The effect of selective absorption of light waves in glazes is accomplished by adding pigments or colorant oxides to their compositions.

In order to determine the conditions for the production of stable-colored glazes opacified by strontium disilicotitanate,

[1] Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.

[2] S. A. Saidvakkosova participated in reducing chromium (VI) from waste chromium electrolyte.

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it is necessary to establish the effect of the pigment of the coating coloring. The conditions of preparation and analysis of glazes with a pigment and the white coatings opacified by fine-disperse crystals of strontium disilicotitanate were identical. The matrix for the colored glaze containing 2% (above 100%) pigments was the strontium-barium glaze composition: (wt.%): 66.05 SiO_2, 4.31 Al_2O_3, 3.27 B_2O_3, 4.00 SrO, 1.30 ZnO, 1.57 K_2O, 5.54 Na_2O, 7.00 TiO_2, and 6.00 BaO [5].

The frit was melted in an electric furnace with silite heaters at a temperature of 1250°C until getting a homogenous melt, then granulated in water and milled together with 2% bentonite to a grain size of 0.063 mm. The glaze moisture in milling was 45%. The glaze was deposited on fired facing tiles made at the Angrenskii Ceramic Works. The tile firing temperature was brought to the respective maximum values (950 – 1000°C with an interval of 50°C) with exposure at the final temperature for 1 h. After a second firing at different temperatures, the color of all glazed samples varied from light green to bright green.

The white coating without pigment had good luster. The introduction of the chromium-bearing pigment had a positive effect on the color of the coating fired at temperatures of 950 – 1000°C. Upon the introduction of the pigment into the glaze, the samples fired at the same temperature had full opacification and good spread and luster.

The color of the coatings was analyzed on a SF-14 automatic spectrophotometer. The color evaluation was substantiated in the following way: for the coating with the chromium-bearing pigment, the prevailing wavelength is 465 – 600 nm and the color purity 22%.

The white glaze without pigment additive has the highest degree of luster: 50.2% and a thermal resistance of more than 8 thermal cycles. The luster of the glaze with the pigment additive is 48.5%.

The introduction of the chromium-containing pigment (whose firing temperature is 950 – 1000°C) improves the microhardness of glaze coatings. Their chemical resistance to 20% hydrochloric acid is 98.74 – 99.82%, and their resistance to 2 N caustic soda solution is 98.76 – 99.25%.

The TCLE of the samples crystallized at 950°C measured at the softening temperature and at 400°C, depending on the frit composition, increases from 69.82×10^{-7} to $72.48 \times 10^{-7}\ K^{-1}$.

The crystallizing capacity of glaze was studied in heating in a silite furnace at temperatures of 700 – 1000°C (with an interval of 50°C). At 700 – 800°C, crystallization is absent, at 850 – 900°C a crystalline film emerges, ands a crystalline crust is formed at 950°C. All compositions exhibit a sintered state at 700 – 750°C, the luster appears at 800 – 850°C, and the volume crystallization is registered at 900°C.

The x-ray phase analysis of experimental glaze frits with 1 h exposure at temperatures of 850 – 950°C indicated that the main opacifying phase, as in the white-colored basic composition, is strontium disilicotitanate $SrO \cdot TiO_2 \cdot 2SiO_2$ (d = 0.320, 0.298, 0.262, 0.251 nm) and barium silicotitanate (d = 0.302, 0.266, 0.257, 0.238, 0.212, 0.186, 0.156 nm).

The developed tinted glaze compositions have improved physicotechnical properties (microhardness, luster) and high chemical resistance (especially, acid resistance); therefore, they are recommended for use as coatings for decorative facing tiles.

The obtained compositions of glaze coatings based on chromium-containing waste were successfully tested on the conveyor line for facing tiles at the Tashkent Works of construction materials.

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